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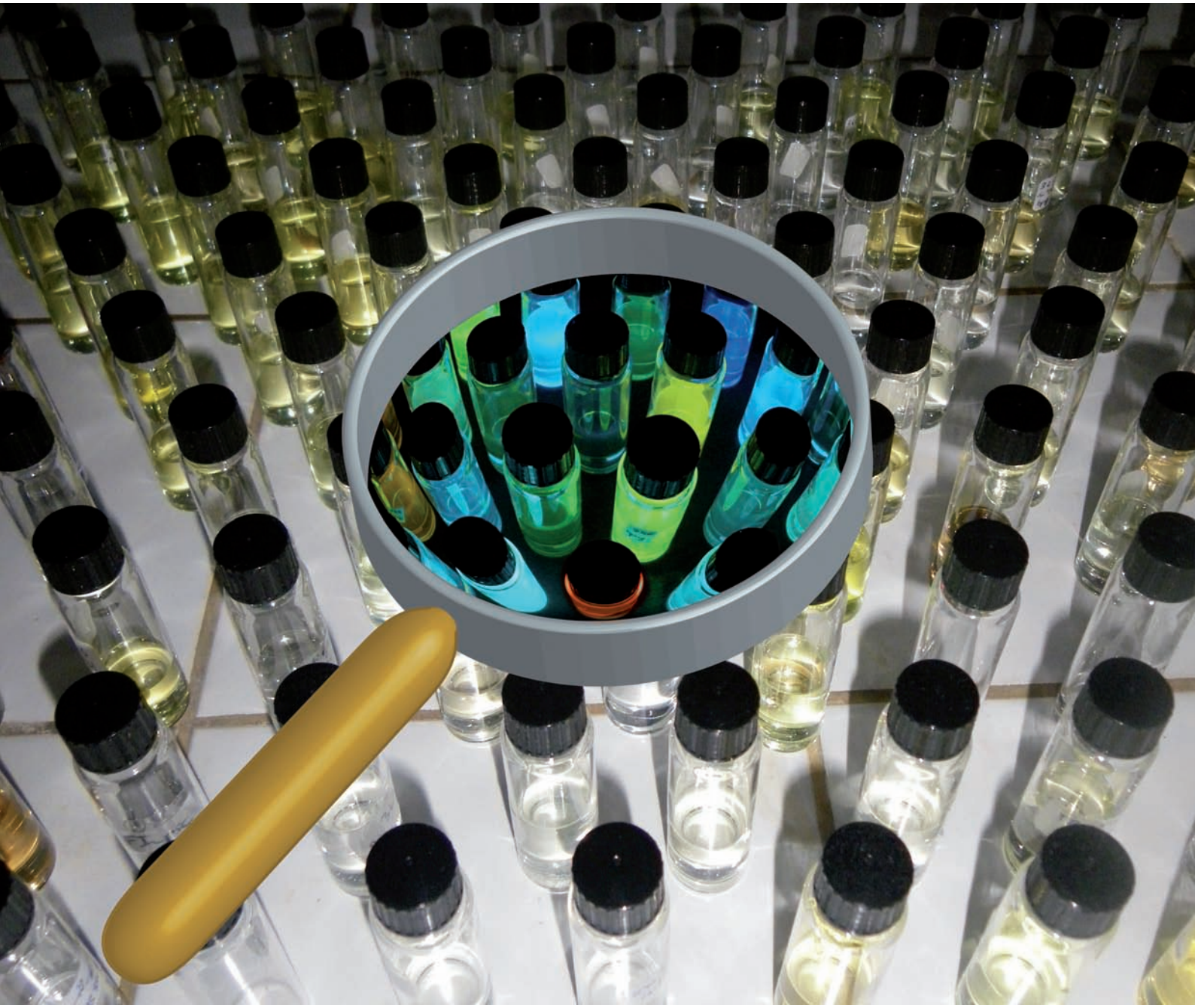

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**PAPER**

# Room-temperature combinatorial screening of cyclometallated iridium(III) complexes for a step towards molecular control of colour purity†

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A library of emission spectra of 90 bis-cyclometallated iridium complexes has been obtained using a simple combinatorial approach performed at room temperature. Trends in emission maxima are rationalized using Hammett parameters and invoking inter ligand energy transfer (ILET) processes. The screening approach allowed us to observe trends in the broadness of emission spectra opening the way for a rational approach to the engineering of the emission colour purity at a molecular level. Finally limitations to the screening strategy are discussed using a case study that involves two different monodentate ligands.

## Introduction

Because of their unique photophysical properties, cyclometallated iridium(III) complexes are attracting widespread interest for applications such as dopants for organic light-emitting diodes (OLEDs),[1–8] light-emitting electro-chemical cells (LEECs),[9–12] luminescent biological labels,[13,14] photocatalysts for hydrogen production,[15] sensitizers for dye-sensitized solar cells,[16] non-linear optics,[17] electro-chemiluminescence[18] and sensors for oxygen,[19–21] fluoride,[22] lead,[23] mercury,[24,25] silver,[26] homocysteine,[27] temperature and pressure.[28] In particular cyclometallated iridium(III) complexes possess high triplet quantum yields and a relatively short radiative lifetime, which are the result of several factors:[29–31] (a) iridium has a large d-orbital splitting compared to other metals in the series; (b) the strong ligand field strength of phenyl anion ligand increases the energy between $t_{2g}$ and $e_g$ orbitals leading to an enhanced gap between the $e_g$ orbital and the LUMO of the ligand; and (c) the close-lying π–π* and MLCT states together with the heavy atom effect enhance the spin–orbit coupling, thus increasing the efficiency of radiative deactivation pathways. Another interesting feature of iridium complexes is the possibility to tune the emission maximum over the entire visible spectrum. The parameters that control this tuning are roughly well understood and have been applied to engineer the emitted light colour in neutral, cationic and anionic complexes. The strategies are ultimately all based on the tuning of the HOMO–LUMO gap, either by using various ligand skeletons or playing with the acceptor/donor character of the substituents, both on the main and the ancillary ligands.[32–45] Finally, for display and lighting applications, the colour purity is an important issue not yet widely addressed from a molecular point of view but with a device engineering approach.[46] The colour purity can be defined as the full width at half maximum (FWHM) of the emission spectra.

Accurate predictions of photophysical properties would be advantageous for developing efficient complexes. However, for example in OLEDs a direct and systematic relationship between photoluminescence in solution and electro-luminescence in solid-state devices is still missing. As a consequence, photoluminescence properties are still considered as a good predictor of electroluminescence properties, despite exceptions to the rule.[47,48] Moreover, the full impact of chemical structures on luminescent properties is not yet fully understood and a lot of theoretical work is being devoted to resolve this issue.[49–53] To examine the impact of chemical modifications on the photophysical properties of the complexes, it is important to synthesize a large series of structurally similar compounds. Combinatorial approaches are very appealing in this respect and have already obtained success with phosphorescent complexes. Lowry *et al.* have shown that it is possible to skip the purification and isolation processes, which are very time consuming, and still get directly from the crude reaction mixture, useful and accurate information about photophysical properties of the desired complex.[54] This allows very small-scale reactions to be run in parallel and therefore dramatically increase of the number of examined complexes in shorter time. Ultimately such libraries of compounds open the possibility to progress in the comprehension of precise structure-property relationships.

However the reported set-up still requires high temperature (150 °C) heating overnight. Since the publication of this combinatorial set-up, progress has been made toward less harsh reaction conditions, typically refluxing in a low boiling solvent like dichloromethane. These new conditions can be applied to the combinatorial method without fundamentally modifying the interest of the approach.

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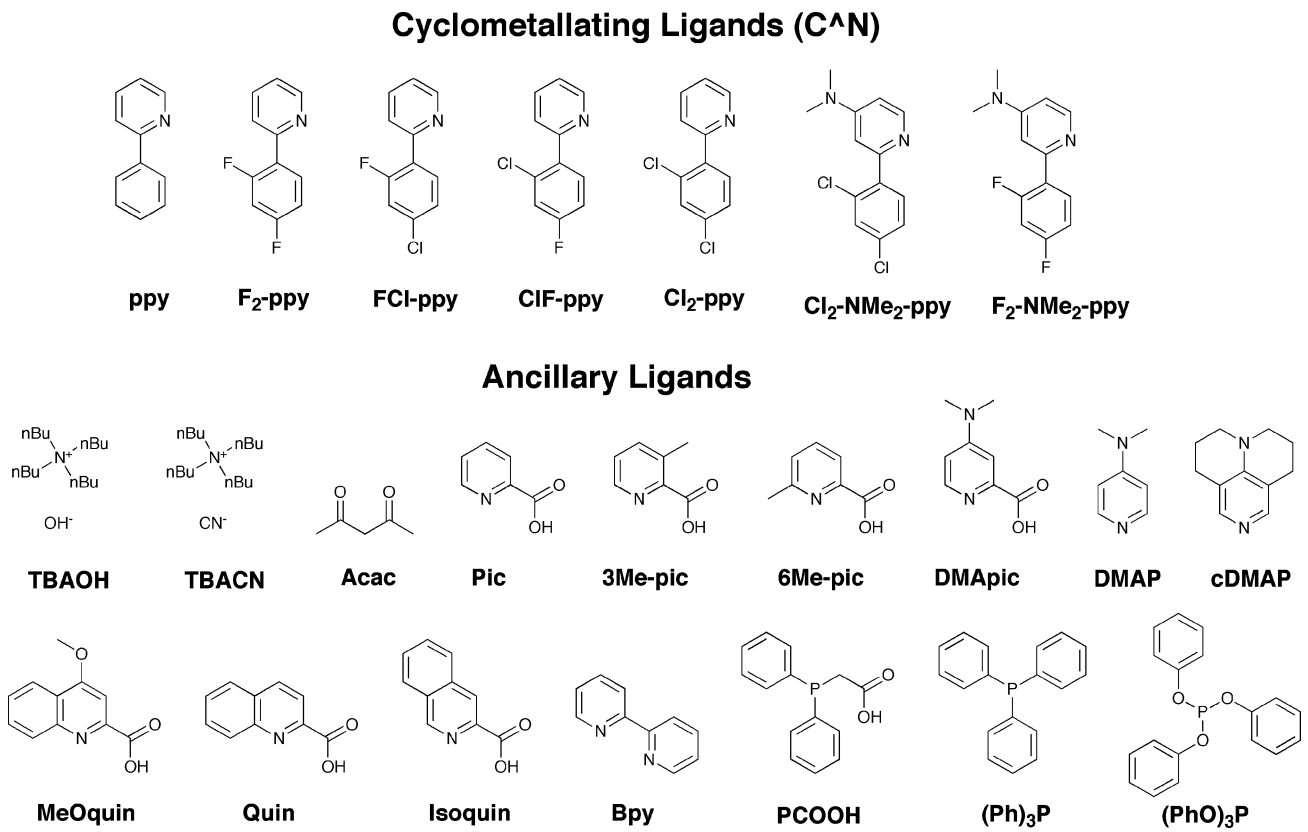


**Scheme 1** Chemical structures of ligands used in this study.

In this report we present a set-up that goes one step further as a library of 90 bis-cyclometallated iridium complexes has been prepared following a combinatorial approach at room temperature (Scheme 1). Traditional synthesis has been used for preparing a small subset of eight complexes to evaluate the validity of the room-temperature approach. As one does not need heating for long hours anymore, we think this work is a valuable practical improvement to the combinatorial approach. First, it is easier to set-up; second, it is safer to leave overnight than a heated closed system; last but not least, it is energetically favourable not to heat at all.

Besides gaining a qualitative understanding of the impact of small structural modifications on emission maxima, our initial interest in the study of the presented library of emission spectra seeks specifically to address the colour purity issue by quickly screening a large amount of compounds. Indeed, we have recently reported a molecule that exhibits very broad emission.[55] The rationalization of this effect was that the LUMO localized on the main ligand, named LUMOm, and the LUMO localized on the ancillary ligand, named LUMOa, are close to being degenerate leading to a cluster of emitting states. Our initial understanding is that by bringing the energy level of the LUMOa closer to the LUMOm, a broadening of the emission spectra should be observed. On the other hand, if a large energy gap exists between the LUMOm and the LUMOa, one should observe a decrease of the FWHM that is to say better colour purity. Testing this hypothesis on a large number of complexes allows generalization of the broadening effect and gives valuable information on how to address the specific problem of colour purity at the molecular level.

### Library preparation and emission trends

For both the combinatorial approach and the traditional syntheses (see ESI†), the chloro-bridged iridium dimers have been synthesized by refluxing $IrCl_3 \cdot xH_2O$ in a 3 : 1 mixture of 2-ethoxyethanol and water in presence of 2.2 equivalents of cyclometallating ligand. Once isolated, stock solutions of dimers, ancillary ligands and tetrabutyl ammonium hydroxide (TBAOH) were prepared in dichloromethane (each solution with a concentration about 0.25 mM). For each combination, 1 mL of dimer solution, 2 mL of ancillary ligand solution and 2 mL of TBAOH solution (or 2 mL of dichloromethane when neutral ligand is used) were mixed in a vial, sonicated for 10 s and left at room temperature on the bench overnight. About 0.5 mL of the solution was then taken and diluted to 5 mL with dichloromethane and emission spectra were directly recorded. It is important to excite at a wavelength higher than 400 nm, preferably close to 450 nm to avoid exciting possible unreacted ancillary ligand. Control complexes have been synthesized and isolated using a classical synthesis that is refluxing in dichloromethane the chloro-bridged iridium dimer with the desired ancillary ligand and in the presence of TBAOH for bidentate anionic ligands.

Screening reactions of dimers using solely TBAOH have been used as a preliminary control for subsequent tests to assess the coordination of the ancillary ligands. Indeed, initial trials with

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larger amounts of TBAOH, in presence of various ancillary ligands, often lead to emission spectra dependant only on the main ligand. Those emission spectra were similar to what is observed with TBAOH alone thus pointing to a similar emitting species that does not contain the ancillary ligand. The exact structure of the complexes formed is at the moment unclear. As silver salts[56] or harsh conditions[57] compared to the room-temperature set-up used in our case are required to replace the chloride with hydroxide, it is expected to be the mono-hydroxy-mono-chloro complex.

The X-ray crystal structures of three control complexes‡, [Ir(2-(2,4-dichlorophenyl)pyridine)$_2$(4-*N*,*N*-dimethylamino-picolinate)]**EB73**, [Ir(2-phenylpyridine)$_2$(picolinate)] **EB183**, and [Ir(2-(2,4-dichlorophenyl)pyridine)$_2$(2-carboxy-4-methoxyquinoline)] **EB95**, have been obtained as well as for the complex [Ir(2-(2,4-difluorophenyl)-4-*N*,*N*-dimethylamino-pyridine)$_2$(4-*N*,*N*-dimethylamino-picolinate)] **N977** (*vide infra*). Typical data are reported in Table 1. The structures exhibit a distorted octahedral geometry around the iridium center with the expected *N*,*N-trans* configuration of the main ligands, Fig. 1.

**Table 1** Selected bond distances (Å) and angles (°)[a]

| | EB73 | EB183 | EB95 | N977 |
|---|---|---|---|---|
| Bond distances | | | | |
| Ir–$N_O$ | 2.042(3) | 2.033(6) | 2.030(2) | 2.032(11) |
| Ir–$N_N$ | 2.036(3) | 2.039(6) | 2.027(2) | 2.027(11) |
| Ir–$N_A$ | 2.135(3) | 2.149(6) | 2.208(2) | 2.174(10) |
| Ir–O | 2.160(2) | 2.149(5) | 2.134(2) | 2.184(7) |
| Ir–$C_O$ | 2.006(3) | 2.002(7) | 1.979(3) | 2.041(13) |
| Ir–$C_N$ | 1.998(3) | 1.996(7) | 2.004(3) | 2.048(13) |
| Bond angles | | | | |
| $C_O$–Ir–$C_N$ | 89.2(1) | 88.5(3) | 86.1(1) | 85.5(5) |
| $C_O$–Ir–$N_N$ | 80.5(1) | 80.2(3) | 79.8(1) | 81.0(5) |
| $C_N$–Ir–$N_O$ | 80.2(1) | 80.8(3) | 80.1(1) | 81.4(5) |
| $C_O$–Ir–$N_A$ | 95.8(1) | 99.8(3) | 105.9(1) | 99.2(4) |
| $C_N$–Ir–O | 98.6(1) | 95.1(2) | 92.3(1) | 98.7(4) |
| $N_O$–Ir–$N_N$ | 172.4(1) | 175.7(2) | 174.5(1) | 176.6(5) |

[a] $N_O$: coordinated nitrogen of the C^N ligand with C *cis* to the oxygen; $N_N$: coordinated nitrogen of the C^N ligand with C in *cis* to $N_A$; $N_A$: coordinated nitrogen of the ancillary ligand; $C_O$: coordinated carbon in *cis* to the oxygen; $C_N$: coordinated carbon in *cis* to $N_A$.

The emission spectra of the control complexes closely match the emission spectra of the corresponding complexes obtained through combinatorial room-temperature set-up (see ESI†). In addition trends of emission maxima follow overall the expectations. Indeed observed emission trends can be rationalized using Hammett parameters $\sigma_m$ and $\sigma_p$[58] and invoking interligand energy transfer (ILET) processes.[59] Starting from 2-phenylpyridine (ppy) as the main ligand and adding two fluorine substituents in positions 2 and 4 on the phenyl group leads to a significant blue shift of the emission for all ancillary ligands utilized. This is a well known approach, arguably the most utilized strategy for blue-shifting the emission maximum. Replacing the fluorine by chlorine leads to a red-shifted emission for all ancillary ligands used but for quinoline and isoquinoline-based ligands. Logically, having one fluorine and one chlorine substituents leads to emission maxima in between emission maxima obtained with difluoro and dichloro substituted complexes. There are no significant differences between 2-chloro-4-fluoro-ppy and

‡ Crystal data for **EB73**: $C_{30}H_{21}Cl_4IrN_4O_2$, *Fw* = 803.51, yellow prismatic, triclinic, space group $P\bar{1}$, *a* = 9.9283(13) Å, *b* = 11.5891(10) Å, *c* = 14.914(3) Å, *α* = 88.213(10)°, *β* = 78.226(13)°, *γ* = 64.844(9)°, *V* = 1517.6(4) Å$^3$, *Z* = 2, $D_c$ = 1.758 g cm$^{-3}$, *F*(000) = 780, *μ* = 4.786 mm$^{-1}$, *T* = 100(2) K, 33984 reflections collected, 6926 independent ($R_{int}$ = 0.0414), $R_1$ = 0.0245, w$R_2$ = 0.0508 [$I > 2\sigma(I)$]. CCDC 803766.Crystal data for **EB183**: $C_{28}H_{20}IrN_3O_2$, *Fw* = 622.67, yellow prismatic, monoclinic, space group $P2_1$, *a* = 9.1602(9) Å, *b* = 14.1871(9) Å, *c* = 9.5929(10) Å, *β* = 117.348(13)°, *V* = 1107.31(18) Å$^3$, *Z* = 2, $D_c$ = 1.868 g cm$^{-3}$, *F*(000) = 604, *μ* = 6.061 mm$^{-1}$, *T* = 140(2) K, 9835 reflections collected, 4283 independent ($R_{int}$ = 0.0367), $R_1$ = 0.0300, w$R_2$ = 0.0728 [$I > 2\sigma(I)$]. CCDC 803764.Crystal data for **EB95**: $C_{33}H_{20}Cl_4IrN_3O_3$, *Fw* = 840.52, yellow prismatic, triclinic, space group $P\bar{1}$, *a* = 10.9629(3) Å, *b* = 11.1318(3) Å, *c* = 12.1713(3) Å, *α* = 90.525(2)°, *β* = 91.673(2)°, *γ* = 102.779(2)°, *V* = 1447.75(7) Å$^3$, *Z* = 2, $D_c$ = 1.928 g cm$^{-3}$, *F*(000) = 816, *μ* = 5.023 mm$^{-1}$, *T* = 140(2) K, 11733 reflections collected, 5655 independent ($R_{int}$ = 0.0167), $R_1$ = 0.0186, w$R_2$ = 0.0472 [$I > 2\sigma(I)$]. CCDC 803767.Crystal data for **N977**: $C_{35}H_{35}F_4IrN_6O_3$, *Fw* = 855.89, yellow prismatic, triclinic, space group $P\bar{1}$, *a* = 9.4762(8) Å, *b* = 13.8917(9) Å, *c* = 15.4205(14) Å, *α* = 108.231(7)°, *β* = 93.780(7)°, *γ* = 107.916(7)°, *V* = 1804.8(3) Å$^3$, *Z* = 2, $D_c$ = 1.575 g cm$^{-3}$, *F*(000) = 848, *μ* = 3.762 mm$^{-1}$, *T* = 140(2) K, 9199 reflections collected, 4465 independent ($R_{int}$ = 0.1066), $R_1$ = 0.0667, w$R_2$ = 0.1024 [$I > 2\sigma(I)$]. CCDC 803768.Crystal data for **EB43**: $C_{40}H_{42}F_{10}IrN_8P$, *Fw* = 1047.99, yellow prismatic, triclinic, space group $P\bar{1}$, *a* = 9.8685(3) Å, *b* = 12.1840(3) Å, *c* = 18.1833(5) Å, *α* = 82.031(2)°, *β* = 74.703(2)°, *γ* = 82.763(2)°, *V* = 2079.33(10) Å$^3$, *Z* = 2, $D_c$ = 1.674 g cm$^{-3}$, *F*(000) = 1040, *μ* = 3.335 mm$^{-1}$, *T* = 140(2) K, 19019 reflections collected, 8132 independent ($R_{int}$ = 0.0194), $R_1$ = 0.0279, w$R_2$ = 0.0715 [$I > 2\sigma(I)$]. CCDC 803765.Crystal data for **N995**: $C_{35}H_{34}Cl_2F_4IrN_7$, *Fw* = 891.79, yellow prismatic, triclinic, space group $P\bar{1}$, *a* = 9.753(5) Å, *b* = 12.791(6) Å, *c* = 15.288(6) Å, *α* = 73.78(3)°, *β* = 85.69(4)°, *γ* = 69.36(3)°, *V* = 1713.2(13) Å$^3$, *Z* = 2, $D_c$ = 1.729 g cm$^{-3}$, *F*(000) = 880, *μ* = 4.112 mm$^{-1}$, *T* = 100(2) K, 22003 reflections collected, 5957 independent ($R_{int}$ = 0.0981), $R_1$ = 0.0879, w$R_2$ = 0.2070 [$I > 2\sigma(I)$]. CCDC 803769.Crystal data for **N995dimer**: $C_{61}H_{54}F_8Ir_2N_{12}$, *Fw* = 1491.56, yellow prismatic, triclinic, space group $P\bar{1}$, *a* = 17.450(2) Å, *b* = 18.5594(19) Å, *c* = 24.439(4) Å, *α* = 80.953(10)°, *β* = 76.281(12)°, *γ* = 68.024(8)°, *V* = 7109.5(16) Å$^3$, *Z* = 4, $D_c$ = 1.394 g cm$^{-3}$, *F*(000) = 2920, *μ* = 3.802 mm$^{-1}$, *T* = 100(2) K, 161099 reflections collected, 31819 independent ($R_{int}$ = 0.0428), $R_1$ = 0.0395, w$R_2$ = 0.0906 [$I > 2\sigma(I)$]. CCDC 803770.

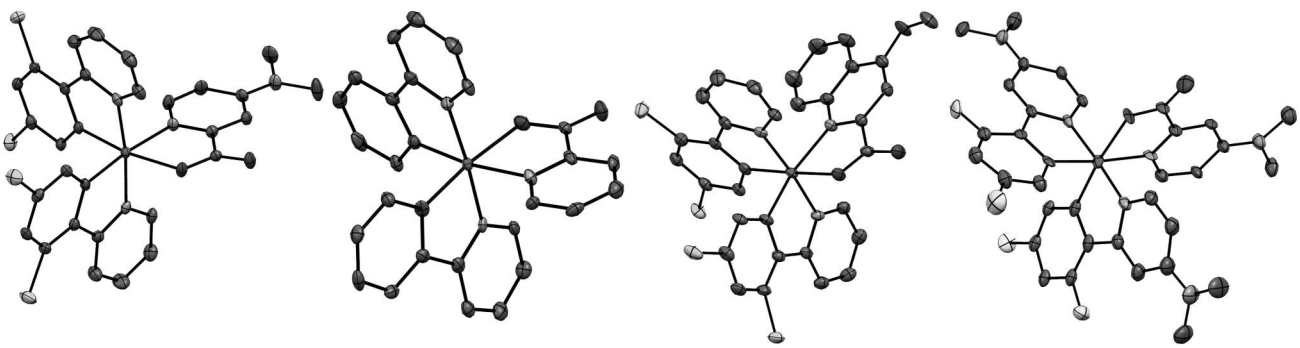

**Fig. 1** X-ray crystal structures of **EB73**, **EB183**, **EB95** and **N977**.

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4-chloro-2-fluoro-ppy pointing to the similarity of the 2 and 4 position for colour tuning, Fig. 2.

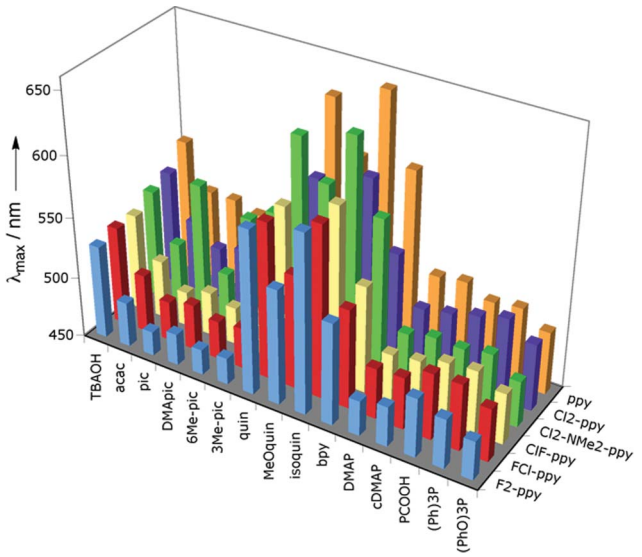


**Fig. 2** Three-dimensional plot for emission maxima from the library.

Generally the HOMO orbital of the complexes contains a large amount of d orbitals from the iridium while the LUMO orbital corresponds mostly to the π* orbitals of the ligand and is localized on the pyridine. One could assume that, based on the position of the halogen substituents, the inductive/mesomeric effects on the *meta* position will mainly influence the energy level of the HOMO orbital while inductive/mesomeric effects on the *ortho*/*para* position will influence the energy level of the LUMO orbital. Indeed the iridium is coordinated to the phenyl ring through the carbon in the *meta* position to the halogen substituents while the pyridine is in *ortho*/*para* position of the halogen substituents. Therefore $\sigma_m$ and $\sigma_p$ can be directly correlated to the energy level of the HOMO and LUMO orbitals, respectively. Using this simplified approach, it is possible to explain most features of the emission trends.

While fluorine has a slightly stronger acceptor inductive effect than chlorine, it has a significantly higher mesomeric donor influence as seen with their respective field and resonance parameters, F and R.[58] The inductive effect of the substituents affects all nearby atoms, simply decreasing as through-bond distance increases. On the other hand, the mesomeric effect influences atoms in the *ortho* and *para* position of the substituents significantly more than atoms in the *meta* position. The resultant of these two effects is apparent in the Hammett parameters $\sigma_m$ and $\sigma_p$: they are 0.34 and 0.06 for the fluorine and 0.37 and 0.23 for the chlorine.[58] Therefore replacing fluorine by chlorine should slightly stabilize the HOMO orbital due to the slightly higher value of the $\sigma_m$ parameter for chlorine and significantly stabilize the LUMO orbital due to the significantly higher value of the $\sigma_p$ parameter for chlorine. Ultimately this decreases the HOMO–LUMO gap, which translates into a red-shift of the emission maximum. In the case of quinoline and isoquinoline based ancillary ligands, the emission is expected to originate from the chromophoric ancillary ligand due to ILET process. This process has been well described by Park and coworkers[37,59] and is based on the relative energy of the triplet of the C^N and the ancillary ligands. If the main ligand has a lower triplet state energy than the ancillary ligand, then emission originates from the main ligand with the LUMO of the complex mostly localized on the C^N ligand. On the other hand, when the energy of the triplet state of the ancillary ligand is lower than the one of the main ligand then emission occurs from the triplet state of the ancillary ligand and the LUMO of the complex is mostly localized on the ancillary ligand. The HOMO–LUMO gap is not controlled anymore only by the substituents on the main ligand but by the HOMO mostly localized on the cyclometallating phenyl and the LUMO on the ancillary ligand. In a first approximation, one can consider the energy of the triplet state of the ancillary ligand to be independent of the rest of the complex. That means that the energy level of the LUMOa is independent of the rest of the molecule. Therefore the blue shifted emission observed for the chlorine-substituted complex compared to the fluorine substituted complex is supporting the stabilization of the HOMO orbital by chlorine compared to fluorine.

In addition to acceptor substituents on the *ortho*-metallated phenyl rings, blue shifted emissions can be obtained by adding donor groups on the pyridine ring. In this case the increased HOMO–LUMO gap is obtained due to larger destabilization of the LUMO orbital than the HOMO orbital. We used dimethyl amino groups as strong donor substituents with both chlorine and fluorine substituents on the phenyl. As expected we observed blue shifted emissions with most of the ancillary ligands used for the screening. However, as the LUMO orbital is strongly destabilized and due to increased $^3$π–π* energy of the main ligand, emission processes involving the ancillary ligand are more prone to be observed. Indeed it is more likely for the $^3$π–π* energy of the ancillary ligand to be smaller than the main ligand and that the LUMO of the complex would be localized on the ancillary ligand. Red emission is indeed observed when picolinate is used as an ancillary ligand. Only if destabilization of the molecular orbitals localized on the ancillary ligand is achieved by strong donor substituents can one observe an overall blue shifted emission. Interestingly, starting from the combination 2-(2,4-dichlorophenyl)pyridine and picolinate and adding a dimethyl amino group onto the pyridine leads to red shifted emission as does adding a dimethyl amino group on the picolinate. Adding a dimethyl amino group on both the pyridine and the picolinate leads to blue shifted emission. Hence one can consider that a red shift plus a red shift leads to an overall blue shift when correctly engineered.

Applying this combination of substituents on the difluoro-substituted ppy ligand we prepared the complex [Ir(2-(2,4-difluorophenyl)-4-*N*,*N*-dimethylaminopyridine)$_2$(2-carboxy-4-*N*,*N*-dimethylaminopyridine)] **N977**. The X-ray crystal structure has been obtained‡ and exhibits the slightly distorted octahedral geometry around the iridium center with *N*,*N*-*trans* configuration for the pyridines of the main ligands (Fig. 1 and Table 1). As expected this is the bluest emission in the bidentate series studied here with highest energy band at 460 nm, only surpassed by the use of monodentate ligands such as triphenyl phosphite (454 nm) and DMAP in **EB43** (*vide infra*, 447 nm). **N977** emission is compared to **FIrPic** emission in Fig. 3. Interestingly it displays broader emission than **FIrPic**, 3755 and 3518 cm$^{-1}$ respectively.

Overall, the close correspondence between emission spectra of complexes from combinatorial synthesis and from the control

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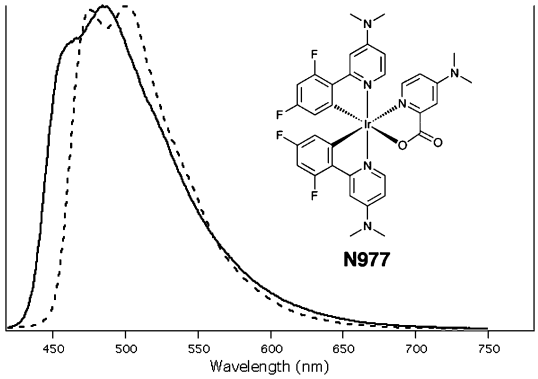


**Fig. 3** Emission spectra of **N977** (solid line) and **FIrPic** from combinatorial approach (dashed line) at room temperature.

synthesis as well as rationalized trends in emission maxima suggest that the combinatorial approach at room temperature is a valid approach for expedient emission screening of iridium complexes. This approach is best applied to bidentate ligands and to single-type monodentate ligands.

### Trends in broadness of emission

While it would be inappropriate to read to much into the broadness of the emission spectra of the library it is possible to find support for our initial hypothesis about the relative energy of the LUMOm and LUMOa. It is best exemplified by looking at the trend of the broadness along the series Acac, DMApic, 3Me-pic and Pic, as ancillary ligand (Fig. 4). In this case, Pic is considered as having the lowest triplet energy. Adding donor substituents of increasing strength (methyl to *N*-*N*-dimethylamino group) should increase the energy of the triplet state of the ancillary ligand. Based on our previous simplification, this corresponds to a destabilization of the LUMOa compared to the LUMOm. As the energy gap between those two molecular orbitals increases, the colour purity of the emission is improved as shown by the decrease of the FWHM. The only exception in this series is 2-(2,4-dichlorophenyl)-4-*N*,*N*-dimethylamino-pyridine where the ancillary ligand 3Me-pic leads to broader emission than with simple Pic. To refine our hypothesis, both MO do not have to be as close as possible but there exists apparently an optimum energetic distance.

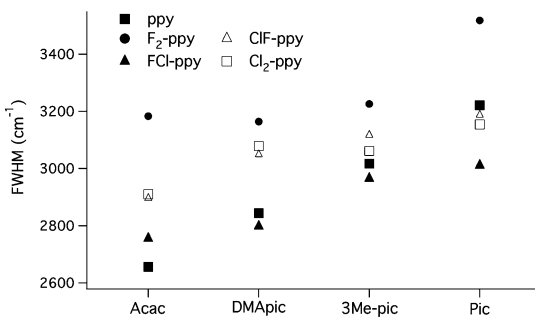


**Fig. 4** Broadness of emission as a function of ancillary ligand in the picolinate series.

The differences observed between FCl-ppy- and ClF-ppy-based dimers are additional exceptions of interest. Similar results for both could have been expected due to similar electronic effects of the 2 and 4 position on the emission maxima. However, compared to FCl-ppy, ClF-ppy leads systematically to broader emission but for ancillary ligands involved in ILET processes. One needs to invoke either a steric effect that disturbs the electronic states of the molecules or the slight electronic difference between the *ortho* and the *para* position.

Overall, the approach considering the relative energy levels of LUMOa and LUMOm is a valuable and simple tool for tuning the colour purity of the emission at the molecular level. While its impact appears significant, the exceptions observed shows that it is obviously not the only parameter at play. In depth study of those exceptions should unravel additional key parameters affecting the colour purity and open the way to a better control of this important, but up-to-now poorly addressed, photophysical property of phosphorescent emitters.

### Limitation of the screening approach

We attempt to extend the scope of the room temperature screening approach to the use of two different monodentate ligands. Complexes of the type $Ir(C^{\wedge}N)_2L^aL^b$, $L^a$ and $L^b$ being monodentate ligands, have been used to tune the emission properties in particular towards the blue.[60–62] In this part of the visible spectrum, small energetic differences induced by the surrounding medium do not translate into large shifts of emission maxima. When we used 4-*N*,*N*-dimethylamino-pyridine and cyanide as neutral and anionic monodentate ligands, we observed few nanometres shift compared to our expectations and poor reproducibility, which attracted our attention. The selected C^N ligand for the control complex was 2-(2,4-difluorophenyl)-4-dimethylamino-pyridine as this is the ligand leading to largest discrepancy in our initial tests with two different monodentate ligands. An additional interest of this ligand is the bluer emission expected compared to other C^N ligands used in this study, as observed with **N977**.

The synthesis of the control complex, **N995**, was initially performed by adding DMAP to the chloro-bridged dimer followed, after stirring overnight at room temperature, by addition of TBACN. However, isolation of the product leads to a complicated mixture as shown by $^1$H NMR. Purifications using column chromatography on silica gel, aluminium oxide or Sephadex (LH-20) as well as attempts to use thin layer chromatography plates lead only to very limited improvement. A representative $^1$H NMR of the **N995** complex obtained with standard synthetic methods and using the various purifications techniques is shown in the ESI.† While the starting chloro-bridged dimer was of good purity the reaction with DMAP at room temperature leads to an intractable mixture. Unexpectedly one of the side products isolated is the complex that has two DMAPs coordinated on the iridium, **EB43** (Scheme 2). This complex can be cleanly obtained by refluxing the chloro-bridged dimer in dichloromethane with an excess of DMAP and was isolated as the hexafluorophosphate salt. This means that the chloride is labile at room temperature. Usually neutral monodentate ligands (L; for example pyridine, carbon monoxide and acetonitrile,[62] phosphine,[60] isocyanide,[61] dimethylsulfoxide[63]) simply break the chloro-bridged iridium dimer leading to the monochloro complex $[Ir(C^{\wedge}N)_2(L)Cl]$ already at room temperature. However silver salts are required to remove the chloride and replace it with a second neutral monodentate ligand. To verify that this effect was not due solely to the DMAP,

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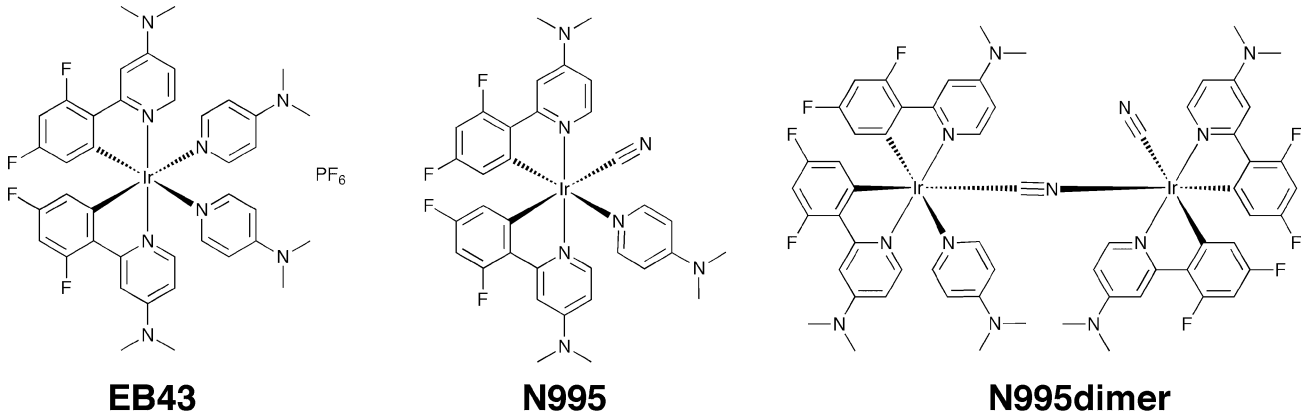


**Scheme 2** Molecular structure of **EB43**, **N995** and **N995dimer.**

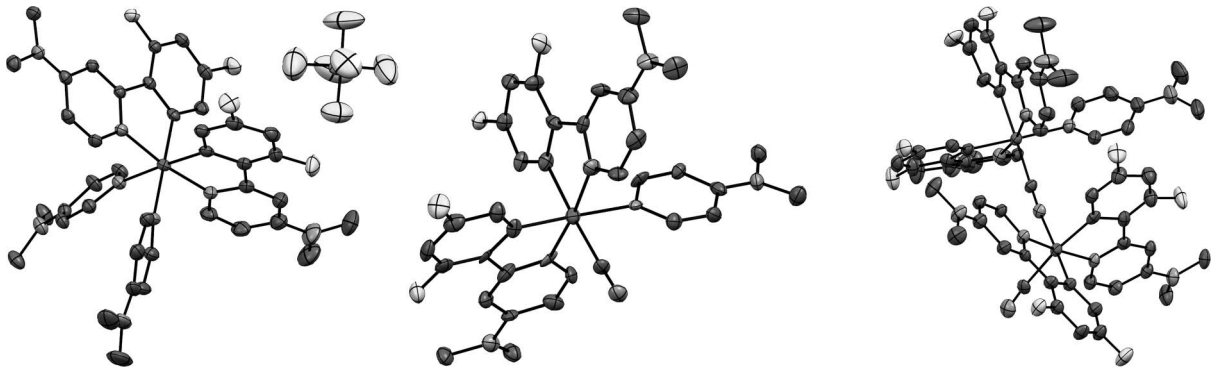

**Fig. 5** X-ray crystal structure of **EB43**, **N995** and **N995dimer**.

we used the chloro-bridged dimer $[Ir(ppy)_2Cl]_2$, that is without substituents on the main ligands. Using the same room temperature conditions leads cleanly to the complex $[Ir(ppy)_2(DMAP)(Cl)]$ contaminated by the excess of DMAP used (see ESI†). No trace of side products was observed.

The lability of the chloride originates therefore from the substituent pattern on the C^N ligand. Both fluorine[64] and *N*,*N*-dimethylamino[65,66] substituents have been shown to favour *N*,*N*-*trans* to *cis* isomerization process in cyclometallated iridium complexes as compared to non-substituted ligands. As isomerization involves the breaking of a bond, the length of this bond can be directly correlated to the facility of being broken. The leaving ability of chloride can be correlated to the length of the Ir–Cl bond. Unfortunately only very few X-ray crystal structures involving an Ir–Cl bond with a cyclometallated ppy ligand are available. Therefore we used complexes with a picolinate as ancillary ligand and compared the lengths of the Ir–O bonds as a proxy for the Ir–Cl bonds of interest. Starting from $[Ir(ppy)_2(picolinate)]$ (**EB183**), the Ir–O bond increases from 2.149(5) to 2.179(2) Å when adding a *N*,*N*-dimethylamino group on the picolinate (**N984**[66]). Going to **N977** further increases the bond length to 2.184(7) Å which shows that this bond is weakened by the substitution pattern. To decrease the leaving ability of the chloride, we added to the reaction mixture a large excess of tetrabutyl ammonium chloride (TBACl). Indeed we hypothesized that as the leaving ability of chloride increases, competition for coordination to the iridium center becomes possible between chloride and DMAP, perhaps leading to some sort of equilibrium. The increased concentration of chloride anion should disfavour the coordination of the second DMAP ligand. While this may be surprising for complexes usually considered as inert, this approach has been successful and the mono-chloro intermediate complex was obtained with improved purity. Subsequent reaction with cyanide cleanly leads to pure **N995** (see ESI†). An X-ray crystal structure has been obtained (Fig. 5). Interestingly, one crystallization attempt which took several weeks to produce single crystals, displays an unexpected dinuclear iridium complex formed *in situ*, **N995dimer** where one cyanide acts as a bridging unit similar to our recently reported tetranuclear iridium complex.[67] It is as if the DMAP of one **N995** complex has been replaced by a second **N995** complex which acts as a monodentate ligand coordinated through the nitrogen of the cyanide.

This labile chloride effect is attributed here to the specific substitution pattern of the C^N ligand and the use of DMAP. Although this is unlikely to be a general case, we didn't pursue the room-temperature combinatorial approach with this class of complex having two different monodentate ligands. The specific use of DMAP-CN combination may still be valuable as $CN_2$, CN-DMAP and $DMAP_2$ complexes have very similar emission maxima (see ESI†).

## Conclusion

In conclusion we have shown that room temperature is sufficient for the combinatorial approach used to swiftly prepare a large library of highly phosphorescent bis-cyclometallated iridium(III)

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complexes in a short time. The library of emission spectra obtained is valuable to assess trends in emission maxima. These trends can be easily explained using Hammett parameters and invoking ILET processes. More important, the library allowed us to refine and generalized our hypothesis about parameters influencing the broadness of emission, which will be used to obtain broadly emitting complexes with improved photophysical properties. This opens new opportunities for addressing the colour purity of emitted light at a molecular level. Finally we evoked the limitation of the screening approach by discussing a specific example showing that in some specific cases bis-cyclometallated iridium complexes are not as inert as initially thought and show promising ability for the preparation of discrete multinuclear species.

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